29445 DUP.

IGM88AP-101-768-G
CNRC 29445

Crystallinity in PPS-Carbon Composites: A Study Using Diffuse Reflection FT-IR Spectroscopy and Differential Scanning Calorimetry

K. C. COLE, D. NOËL, J.-J. HECHLER, D. WILSON*

Industrial Materials Research Institute, National Research Council Canada
75, bd de Mortagne, Boucherville, Québec, Canada J4B 6Y4

**Canadair Ltd.*
P. O. Box 6087, Station A, Montréal, Québec, Canada H3C 3G9

Synopsis

A method based on diffuse reflection Fourier transform infrared (FT-IR) spectroscopy has been developed for determining the state of crystallinity in composite materials made from polyphenylene sulfide (PPS) reinforced with carbon fibers. Using this technique, good-quality spectra can be rapidly obtained directly from the surface of prepreg or molded composite. Several peaks in the spectrum are sensitive to the crystallinity and can be used for quantitative characterization purposes. The recommended indicator is the ratio of the heights of the peaks at 1075 and 1093 cm^{-1}. Using a range of samples of varying crystallinity prepared by annealing amorphous prepreg, it has been shown that there is a very good correlation between this ratio and the enthalpy of crystallization as determined by differential scanning calorimetry. The effects of such annealing, as well as heating in air at high temperatures, have been investigated.

Keywords: Polyphenylene sulfide, crystallinity, infrared spectroscopy, differential scanning calorimetry, PPS, FT-IR, DSC.

INTRODUCTION

In the rapidly expanding field of high-performance composites, there is increasing interest in replacing thermoset polymer matrices by engineering thermoplastics such as polyether ether ketone (PEEK) and polyphenylene sulfide (PPS). One important advantage of these materials compared to thermosets such as epoxies and polyimides is that they are non-reactive systems. Furthermore, they generally provide better impact strength (toughness), better high-temperature performance, better resistance to solvents and other chemicals, lower moisture absorption, and better flame resistance. Disadvantages associated with thermoplastics include their rigidity, the high temperatures required for processing, and the importance of controlling their degree of crystallinity.

The properties, processing, and applications of PPS have been described in recent articles.[1-3] The physical properties of a part made from PPS are affected by the degree of crystallinity, which may vary from less than 10% to greater than 60%, depending on the thermal history.[3] In view of the importance of the degree of crystallinity and its dependence upon processing conditions, it would be desirable to have a fast and reliable method for determining the crystallinity in a finished part. Information concerning crystallinity can be obtained through a number of instrumental methods, including X-ray diffraction, differential scanning calorimetry, and transmission infrared spectroscopy. Recently, we have demonstrated the possibilities of using diffuse reflection (DR) Fourier transform infrared spectroscopy for examining the surface of prepregs and composites containing carbon fiber reinforcement.[4] The main advantages of this method are rapidity and ease of sample preparation. The object of this paper is to demonstrate the usefulness of diffuse reflection FT-IR for providing information on the crystallinity of PPS in PPS-carbon composites.

Several papers have been published concerning crystallinity in PPS.[5-17] In a study of commercial PPS, Brady[6] used X-ray diffraction to determine a "crystallinity index" C_i which was taken to be a good approximation to the true degree of crystallinity. Rapid quenching of molten polymer gives a material with very low crystallinity ($C_i \leq 5\%$). When this is heated at temperatures above 121°C, crystallization occurs rapidly, resulting in a maximum degree of crystallinity

of about 65%. In quenched moldings one-eighth inch thick, a crystallinity gradient was observed, with C_i ranging from about 5% at the surface to 40-50% at the centre. The rate of crystallization was found to be extremely slow at 93°C, moderately fast at 107°C, and quite fast above 121°C. Other studies[9,10] have shown that the maximum rate is observed around 170-180°C, which is about halfway between the glass transition temperature (T_g = 85°C) and the crystalline melting point (T_m = 285°C). The presence of reinforcing fibers has been shown to accelerate the crystallization.[8,10] Certain solvents can also induce crystallization in amorphous PPS,[11] and the effects of annealing at different temperatures have recently been reported.[13,17]

There have been several reports of the infrared spectrum of PPS,[6,7,17-27] almost always involving the pure material in the form of either a very thin film or a fine powder. Spectra have been measured in transmission, attenuated total reflection, and specular reflection, but not in diffuse reflection. A table summarizing results from different papers, together with a tentative band assignment, is given by Radhakrishnan and Nadkarni.[7]

One important point concerning polyphenylene sulfide is that, although it is generally considered to be a thermoplastic, it also possesses some thermoset character. When it is heated in air at temperatures above or slightly below its melting point, it undergoes structural changes involving chain extension, branching, and crosslinking.[6,8,12,19,27] This results in a higher apparent molecular weight and a lower ultimate degree of crystallinity.[6] It also affects the crystalline morphology, the chemical resistance, and the mechanical properties,[8] as well as the infrared spectrum.[19]

EXPERIMENTAL

The prepreg studied was Ryton AC40-60 made by Phillips Petroleum Company, Bartlesville, Oklahoma, U.S.A. It contains long carbon fibers arranged in a unidirectional manner and impregnated with high-molecular-weight PPS. The nominal fiber content is 60% by weight. The thickness (average of 10 measurements) was 218 μm, with a relative standard deviation of 3%.

A molded panel was made by laying up 4 plies of prepreg, placing them in an aluminum mold, heating to 315°C (600°F), pressing at 1.03 MPa (150 psi) for 5 min, then cooling at a rate of 11°C (20°F) per minute. The final thickness was around 700 μm.

Prepreg samples with varying degrees of crystallinity were prepared by isothermal annealing of the highly amorphous prepreg in a forced air convection oven maintained at the required temperature. Two aluminum blocks were placed in the oven and allowed to equilibrate. A strip of prepreg about 1 cm x 5 cm was then placed between the heated blocks. After the desired interval the strip was removed and quickly quenched in liquid nitrogen. This minimizes the time required for heat transfer to and from the sample in order to avoid a gradient in crystallinity from the surface to the centre. Such effects are not expected to be large because the prepreg samples are quite thin. However, it is important to avoid them because diffuse reflection FT-IR sees only the surface of the specimen, whereas DSC measures the whole sample. Each quenched strip was cut into 5 pieces about 1 cm x 1 cm. Of these, the three central ones were used for infrared analysis followed by differential scanning calorimetry.

Infrared spectroscopic measurements were made on a Nicolet 170SX Fourier transform instrument equipped with a mercury cadmium telluride detector and a "praying mantis" type diffuse reflection accessory from Harrick Scientific Corporation. Powdered compacted potassium bromide was used as a reference material, and spectra were recorded using an accumulation of 128 scans.

Differential scanning calorimetry was done on a SETARAM Model CDP111 instrument using paired aluminum crucibles. The sample size was usually around 75 mg, and the temperature was programmed to increase at a rate of 5°C per minute.

RESULTS AND DISCUSSION

Initial Experiments

Infrared Spectroscopy. Figure 1 shows diffuse reflectance infrared spectra of the carbon-PPS prepreg, as received, for different sample orientations with respect to the infrared beam direction. Because the fibers in the prepreg are aligned unidirectionally, the orientation of the sample in the diffuse reflection accessory has an effect on the quality of the spectrum. The best result is obtained with the fiber direction parallel to the beam direction of the instrument, and all subsequent spectra were measured using this orientation. The dependence on orientation is related to the optical design of the reflection accessory, and may be different for other configurations.

The spectrum shows a fairly strong continuous background absorption resulting mainly from the carbon fibers. Although there are a few weak peaks in the 3100-3000 cm^{-1} region corresponding to C-H stretching vibrations, most of the information of interest is contained in the low-frequency region between 2000 and 400 cm^{-1}. In order to make full use of this information, certain manipulations are necessary. The first is the calculation of the Kubelka-Munk function, according to the following equation:

$$F(R) = \frac{k}{s} = \frac{(1 - R)^2}{2R} \qquad (1)$$

where R is the diffuse reflectance, k is the absorption coefficient of the sample, and s is a scattering coefficient. Of these, the absorption coefficient k is of greatest interest, since it is the quantity which determines the transmission spectrum. The scattering coefficient varies only gradually with frequency. Although the Kubelka-Munk model does not strictly apply to the present case (it was derived for the case of an isotropically-scattering powder), it has been found[4] that for carbon-fiber prepreg the Kubelka-Munk transformation gives a better match to the true spectrum than does the pseudo-absorbance transformation $A = -\log_{10}R$. The second manipulation performed is a baseline correction to take account of the background absorption due to the carbon. Figure 2 shows spectra

obtained in this way for the initial prepreg (low degree of crystallinity) and the molded 4-ply panel (high crystallinity). (The state of crystallinity was confirmed by DSC as described in the next section.) The prepreg spectrum is in excellent agreement with reported transmission spectra of pure PPS, expressed in absorbance units.[21,22] It should be noted that the diffuse reflection technique "sees" mainly the very thin surface layer lying above the carbon fibers. As a result, the amount of sample absorbing is small and even the most intense absorption peaks are well-defined, which is not the case in many transmission spectra. It is also interesting to note that the peaks show no evidence of deformation arising from front-surface (Fresnel) reflection, which sometimes causes problems in DR spectra.[4]

Comparison of the spectra of the prepreg and the molded panel in Figure 2 shows several differences, which are best seen by computer subtraction to generate the difference spectrum. It can be seen that crystallization produces an increase in intensity, and sometimes narrowing, of several bands, namely those at 1900, 1474, 1389, 1093, 1011, 961, 813, 557, and 484 cm^{-1}. Some of these also show a significant frequency shift (1900 to 1907, 813 to 820). The bands at 1574, 1180, and 1075 cm^{-1}, on the other hand, do not appear to be affected. The spectra given here and the changes which occur on crystallization are in agreement with previous work.[6,17,22]

Differential Scanning Calorimetry. Figure 3 shows the DSC thermograms of the two samples just described; they resemble those reported in the literature.[6,10] The difference in crystallinity between the two is obvious. The initial prepreg shows the three features characteristic of amorphous PPS: (i) the glass transition around 83°C; (ii) an exothermic peak at 124°C, corresponding to crystallization of amorphous material; (iii) an endothermic peak at 278°C, corresponding to melting of the crystallized material. For the molded panel, only the melting peak can be seen, which indicates that this sample had already achieved maximum crystallinity. In the initial prepreg, the area of the crystallization peak is about two-thirds of that of the fusion peak, indicating a relatively low initial degree of crystallinity. To obtain absolute values for the degree of crystallinity would require X-ray diffraction work. However, values can be estimated through comparison with the literature. Based on extrapolation of Brady's data[6], the heat of fusion of 100%

crystalline PPS is estimated to be 80 J/g.[9] For the initial prepreg, assuming a PPS content of 40% by weight, the heat of fusion of the PPS after crystallization was found to be 38.4 J/g with a standard deviation of 1.0 J/g. This would correspond to a maximum crystallinity index of around 48%, which is very similar to the figure of 51% reported by Johnson and Ryan[11] from X-ray diffraction work on slow-cooled PPS-carbon composite. The area under the crystallization peak at 124°C corresponds to 25.6 J/g, on which basis the crystallinity index of the initial prepreg is estimated to be 16%.

Quantitative Treatment. In infrared spectroscopy, peak heights are often used for quantitative analysis of composition or other properties. In cases where the exact amount of sample absorbing cannot be determined, it is necessary to use ratios. An experiment was done to check the reproducibility of the diffuse reflectance spectra. Three samples from the initial prepreg and five from the molded panel were measured, and the spectra treated as described previously. Peak heights were measured with respect to baselines drawn between the valleys on either side, and various ratios were calculated. For certain pairs of peaks which overlap (1093 and 1075, 961 and 945, 557 and 484 cm^{-1}), the baseline was chosen to include both peaks. The results are summarized in Table 1. The last column shows the relative change observed on going from the highly amorphous prepreg to the fully crystallized molded panel. Although the biggest percentage change is observed for the 945/961 ratio, it is not considered the best one to use because these bands are quite weak in the DR spectra. In a spectrum of poorer quality, as might result from a sample in which the fibers are not aligned unidirectionally, the error could be significantly higher because of the lower signal-to-noise ratio. The 557/484 ratio is rejected because of the large errors associated with it. Of the four remaining ratios which show significant change, the 1075/1093 ratio is preferred for the following reasons: (i) the peaks are of moderate intensity; (ii) the percentage change in their ratio on crystallization is substantial (– 41%); (iii) the two peaks are very close together, so the effects of any variation of the scattering coefficient with respect to frequency will be minimized; and (iv) the heights of both peaks are calculated using the same baseline, drawn between 1150 and 1040 cm^{-1}.

To check the effect of the fiber orientation on the IR ratio, calculations were also done for the worst possible case, namely fibers perpendicular to the beam direction. Three specimens were measured for the initial prepreg and three for the molded panel. The calculated ratios based on the 1075 and 1093 cm^{-1} bands were 0.740 (σ = 0.032) and 0.459 (σ = 0.035) respectively. In spite of the much poorer quality of the spectra, these agree quite well with the values obtained for the parallel orientation (Table 1). Thus it appears that the method can be applied to any PPS-carbon composite, and does not require a unidirectional fiber orientation.

Annealed Samples

Samples with a range of degrees of crystallinity, prepared by isothermal annealing as described in the Experimental Section, were analyzed quantitatively by FT-IR and DSC. In most cases the results are an average over three specimens. In FT-IR the ratio of the peaks at 1075 and 1093 cm^{-1} ranged from 0.44 to 0.74 with a typical standard deviation of 0.02. For the DSC curves, the enthalpy of crystallization ΔH_c was calculated from the area of the exothermic peak near 124°C, when this peak was present, and the enthalpy of fusion ΔH_m from the endothermic melting peak near 278°C. These values were corrected to 100% PPS assuming a carbon content of 60% by weight. The standard deviation for three specimens was generally less than 1 J/g.

The first experiment was done at 100°C, with samples annealed for periods of 20, 40, 60, and 70 minutes. Neither FT-IR nor DSC could detect any significant changes in these samples. At 100°C, crystallization is very slow.

Subsequent experiments were done at 105°C and 110°C. Figure 4 shows how the IR ratio changes as a function of annealing time. At 105°C, an S-shaped curve is observed, with the greatest changes occurring between 40 and 80 minutes. At 110°C there is a substantial drop in the first forty minutes, followed by a levelling off at a value of around 0.53. It is interesting to note that this limiting value is higher than that found for the molded panel (0.44), indicating a somewhat lower degree of crystallinity. This is in keeping with the observation of Johnson and Ryan[11] that

"When the sample is quenched into the amorphous state and subsequently annealed and crystallized, the crystallinity of the matrix is substantially lower than a slowly cooled and crystallized sample.".

Figure 5 shows the evolution of the DSC thermogram for the samples annealed at 105°C. As the degree of crystallinity increases due to annealing, the primary crystallization peak at 124°C becomes less intense and the maximum shifts slightly to lower temperature (120°C for the 60-minute sample). In the 80-minute and 100-minute samples, it seems to have disappeared, but there remains a residual feature whose origin is not clear at this point. In the 100-minute sample, it appears to be an endothermic peak at 116°C. In all the curves, the melting peak remains virtually unchanged at 278°C.

Figure 6 gives the thermograms for the samples annealed at 110°C. The behaviour is similar to that observed at 105°C, except that the primary crystallization peak has disappeared after only 40 minutes. The same residual feature is observed but it occurs at slightly higher temperature (123°C in the 80-minute sample).

Figure 7 shows the variation with annealing time of the enthalpy of crystallization ΔH_c. Although the number of points is limited, the same trends can be seen as were observed for the FT-IR peak ratio. To examine the correlation between the two, the IR peak ratios were plotted against the ΔH_c values for the series of samples annealed at 105°C. As can be seen in Figure 8, there is an excellent correlation, for which linear regression gives the following equation (squared correlation coefficient 0.983):

$$\text{IR Ratio } (1075/1093\ \text{cm}^{-1}) = 0.442 + 0.0117\ \Delta H_c\ (\text{J/g}) \qquad (2)$$

The close relationship between the IR ratio and the degree of crystallinity is confirmed by the fact that the intercept, which corresponds to $\Delta H_c = 0$ or maximum crystallinity, is the same (within experimental error) as the value found for the highly crystalline molded panel (0.435).

Assuming a linear relationship between ΔH_c and the crystallinity index C_i as estimated above based on Brady's data, it is possible to derive the following expression for C_i in terms of the IR ratio R:

$$C_i\ (\%) = 95 - 106\ R \qquad (3)$$

However, this equation should only be considered *very* approximate since it has not been verified by X-ray diffraction work.

The enthalpy of fusion for the annealed samples varied from 35.4 to 38.2 J/g, very similar to the value of 38.4 J/g observed for the initial prepreg. The slight variation may be due to a variation in the exact amount of PPS present in the different specimens analyzed.

A further experiment was done in which samples were annealed for one hour at different temperatures up to 180°C. The variation of the IR ratio is shown in Figure 9. At 100°C, there is no change from the initial prepreg, but at higher temperatures substantial crystallization occurs. At 180°C, it is virtually complete and the ratio is the same as for the molded panel. DSC curves for these samples are given in Figure 10 and are particularly interesting. They all show the same residual feature mentioned previously, but now it appears at higher temperature and is better defined. It is an endothermic peak, and in almost all cases occurs about 15°C higher than the annealing temperature. This phenomenon has also been reported very recently by others.[13] Apparently isothermal annealing induces a secondary type of crystallization, giving rise to a structure intermediate between the original crystallites and the noncrystalline regions. This "partially ordered" structure "melts" at a temperature slightly above the annealing temperature. Similar behaviour has been observed in PEEK[17] and polyethylene terephthalate.[28]

High-Temperature Treatment

An experiment was done to determine the effects of high-temperature treatment on the prepreg and the DR spectrum. Two strips were placed in a muffle furnace at 320°C in a static air

atmosphere. After 80 minutes, one was quenched in liquid nitrogen. The other was left in the furnace for another hour with the power turned off and the door open, in order to achieve slower cooling.

The DSC curves are shown in Figure 11, together with that of the unheated prepreg. Significant changes occur on heating. For the quenched material, the glass transition occurs around 93°C, about 10° higher than in the initial prepreg. A strong primary crystallization peak is observed at 136°C, also higher than in the untreated prepreg. The melting peak, however, occurs about 10° lower, at 269°C, and the enthalpy of fusion is 31.5 J/g, about 18% lower. Obviously heating above the melting point in air produces structural changes resulting in a lower ultimate degree of crystallinity. The enthalpy of crystallization is 21.0 J/g, indicating that the quenched sample is not completely amorphous. For the slowly cooled sample, no glass transition or crystallization peak is detected, showing that complete crystallization has occurred. However, the melting peak occurs at even lower temperature (250°C) and the heat of fusion is only 23.3 J/g. Apparently more structural changes occurred during the slow-cooling period, further lowering the ultimate degree of crystallinity, which is estimated from ΔH_m to be about only 29%.

The changes observed in the DSC curves on heating the prepreg in air at 320°C are similar to those reported by Ma et al.,[12] although the details are different because of the different conditions used. The changes are attributed to cross-linking, partly through aryl ether linkages. When heating is done in a nitrogen atmosphere, the changes are much smaller, if not negligible, and the predominant reaction is believed to be chain extension rather than cross-linking.[27]

The IR spectra of the prepreg heated in air at 320°C are shown in Figure 12. Comparison with Figure 2 shows no evidence of significant oxidation, although two extremely weak peaks at 1150 and 1050 cm^{-1} could be due to sulfone ($-SO_2-$) and sulfoxide ($-SO-$) groups respectively.[29] The changes reported by other workers,[19,23,27] generally attributed to aryl ether groups and changes in aromatic ring substitution patterns, were not observed here, possibly because the spectra are of lower overall intensity. In Figure 12, the spectrum obtained by subtraction of the quenched material from the more crystalline slowly-cooled material shows the same peaks as Figure 2,

although they are not as well defined. For the quenched sample, the IR 1075/1093 peak ratio is equal to 0.76. This is much the same as for the initial prepreg; both have a high content of amorphous material. However, the slowly cooled sample gave 0.63, which is quite different from the value of 0.44 obtained for the molded panel of Figure 2. This is because the ultimate crystallinity is much lower as a result of the heat treatment. Substitution of 0.63 in Equation (3) gives an index of 28%, quite close to the value estimated from the DSC result.

At temperatures up to 180°C the effects of heating in air appear to be negligible, since the DSC melting point remains at 278°C (Figure 10). Also, samples annealed at 180°C under vacuum gave the same FT-IR and DSC results as those annealed in air.

Comparison with Other Work

Udipi[26] and Kaul[30] have recently reported a study of the chemical oxidation of PPS using peracids. The oxidation produces substantial changes in the FT-IR spectrum due to the formation of sulfoxide and sulfone groups.[26] It was suggested that the band at 1070 cm^{-1} in the starting material indicates the presence of a certain amount of sulfoxide groups. If this were true, it would invalidate the method developed in this work involving the ratio of the 1075 and 1093 cm^{-1} bands, because the intensity of the former would vary with the state of oxidation of the sample. However, there is evidence to indicate that this is not the case. Firstly, the band at 1070 cm^{-1} is present in all the spectra reported in the literature, with much the same relative intensity.[7,18-22] If it were due to oxidation, it would be expected to vary depending on the history of the sample. Secondly, the Raman spectrum of PPS also shows a strong band at 1073 cm^{-1} which has been attributed to an aromatic-sulfur stretching vibration.[22] Thirdly, in the spectra reported by Udipi,[26] this band does not change in intensity upon oxidation. However, a new distinct band appears at around 1050 cm^{-1}, and it is this which should be attributed to sulfoxide groups.[29] Other bands related to oxidation appear at 1325, 1290, and 1155 cm^{-1}; the first and the the third can be assigned to sulfone groups.

Radhakrishnan and Nadkarni[7] studied the molding of PPS powder under high pressure at 30°C. They found that the infrared spectrum changed significantly in the region 800-600 cm^{-1}, and suggested that this might be due to a modification of the crystallinity and to some extent the chemical bonding due to high pressure molding. Figure 13 shows the IR spectra in this region for the samples studied in this work. It is seen that the spectrum is affected very little, either by changes in crystallinity or by the changes induced on heating at 320°C in air. Thus the results obtained here offer no explanation for those of Radhakrishnan and Nadkarni. It would appear that such changes, if they apply in the present case, have already occurred during the prepreg manufacturing process. They cannot be explained by a simple variation in crystallinity.

CONCLUSIONS

Diffuse reflection Fourier transform infrared spectroscopy can be used to obtain good quality spectra directly from the surface of composite materials based on polyphenylene sulfide reinforced with carbon fibers. For samples in which the fibers at the surface have a preferential direction, the quality of the spectrum depends on the orientation of the sample.

The intensity of several bands in the spectrum varies with the state of crystallization and can be used as a quantitative measure of the absolute degree of crystallinity, for quality control purposes. The recommended indicator is the ratio of the peaks at 1075 and 1093 cm^{-1}. For thin amorphous PPS prepreg annealed at 105°C, there is a good linear correlation between this ratio and the enthalpy of crystallization as measured by differential scanning calorimetry. The crystallinity determined by the IR method is that of the thin surface layer of PPS. For some applications (for example, where solvent resistance is important), this is more important than the bulk crystallinity. For other applications, where the bulk crystallinity is important, the surface crystallinity may in many cases be taken as a minimum value, since the internal crystallinity is expected to be higher because of slower cooling.

In addition to the primary crystallization, corresponding to a DSC peak at 124°C and a melting point of 278°C, isothermal annealing induces a secondary type of crystallization which gives a structure whose "melting point" is about 15°C higher than the annealing temperature.

Heating PPS in air at temperatures near its melting point causes structural changes resulting in a lower ultimate degree of crystallinity and a lower melting point.

ACKNOWLEDGEMENT

The authors would like to thank André Pilon for technical assistance.

REFERENCES

1. C.-C. M. Ma, J. E. O'Connor, and A. Y. Lou, *SAMPE Q.*, **15** (4), 12 (1984).

2. R. S. Shue, *Developments in Plastics Technology*, **2**, 259 (1985).

3. A. J. Klein, *Advanced Materials and Processes*, **2** (8), 20 (1986).

4. K. C. Cole, D. Noël, and J.-J. Hechler, *Polym. Compos.*, **9** (6), (1988) (in press).

5. B. J. Tabor, E. P. Magré, and J. Boon, *Eur. Polym. J.*, **7**, 1127 (1971).

6. D. G. Brady, *J. Appl. Polym. Sci.*, **20**, 2541 (1976).

7. S. Radhakrishnan and V. M. Nadkarni, *Polym. Eng. Sci.*, **24**, 1383 (1984).

8. H. Zeng and G. Ho, *Angew. Makromol. Chem.*, **127**, 103 (1984).

9. A. J. Lovinger, D. D. Davis, and F. J. Padden Jr., *Polymer*, **26**, 1595 (1985).

10. J. P. Jog and V. M. Nadkarni, *J. Appl. Polym. Sci.*, **30**, 997 (1985).

11. T. W. Johnson and C. L. Ryan, *Int. SAMPE Symp. Exhib.*, **31**, 1537 (1986).

12. C.-C. M. Ma, J.-T. Hu, W.-L. Liu, H.-C. Hsia, B.-Y. Shieh, and R.-S. Liu, *Int. SAMPE Symp. Exhib.*, **31**, 420 (1986).

13. P. H. Lindenmeyer, N. T. Gerken, and C. H. Sheppard, *Int. SAMPE Tech. Conf.*, **18**, 45 (1986).

14. J. Garbarczyk, *Polym. Commun.*, **27**, 335 (1986).

15. A. J. Waddon, M. J. Hill, A. Keller, and D. J. Blundell, *J. Mater. Sci.*, **22**, 1773 (1987).

16. A. J. Lovinger, F. J. Padden Jr., and D. D. Davis, *Polymer*, **29**, 229 (1988).

17. C.-L. Ong, W.-L. Chung, M.-F. Sheu, and J.-H. Lin, *Int. SAMPE Symp. Exhib.*, **33**, 1307 (1988).

18. G. F. L. Ehlers, K. R. Fisch, and W. R. Powell, *J. Polym. Sci. Part A-1*, **7**, 2955 (1969).

19. R. T. Hawkins, *Macromolecules*, **9**, 189 (1976).

20. A. Zuk, M. Wejchan-Judek, and E. Rogal, *Polymer*, **19**, 438 (1978).

21. L. W. Shacklette, R. L. Elsenbaumer, R. R. Chance, H. Eckhardt, J. E. Frommer, and R. H. Baughman, *J. Chem. Phys.*, **75**, 1919 (1981).

22. T. C. Clarke, K. K. Kanazawa, V. Y. Lee, J. F. Rabolt, J. R. Reynolds, and G. B. Street, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 117 (1982).

23. S. G. Joshi and S. Radhakrishnan, *Thin Solid Films*, **142**, 213 (1986).

24. K. F. Schoch Jr. and J. Bartko, *Polymer*, **28**, 556 (1987).

25. L. Kreja and A. Warszawski, *J. Mater. Sci.*, **23**, 497 (1988).

26. K. Udipi, *Polymer Preprints*, **28**, 217 (1987).

27. C.-C. M. Ma, L.-T. Hsiue, W.-G. Wu, W.-L. Liu, and J.-T. Hu, *Int. SAMPE Symp. Exhib.*, **33**, 652 (1988).

28. A. O. Kays and J. D. Hunter, *ASTM Special Technical Publication*, **797**, 119-132 (1983).

29. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules, 3rd Ed.*, Chapman and Hall, London, 1975.

30. A. Kaul, *Polymer Preprints*, **28**, 229 (1987).

Table 1. Peak height ratios obtained from diffuse reflectance spectra.

Peaks Ratioed (Positions in cm^{-1})	Initial Prepreg		Molded Panel		Change
	Avg.	Std. Dev.	Avg.	Std. Dev.	
1574/1474	0.474	0.031 (6.6%)	0.337	0.060 (17.7%)	– 29%
1389/1474	0.441	0.017 (3.9%)	0.429	0.057 (13.3%)	– 3%
1574/1389	1.074	0.033 (3.0%)	0.784	0.070 (8.9%)	– 27%
1075/1093	0.733	0.009 (1.2%)	0.435	0.032 (7.3%)	– 41%
1093/1011	0.984	0.037 (3.8%)	0.955	0.069 (7.2%)	– 3%
1075/1011	0.721	0.031 (4.3%)	0.414	0.016 (3.8%)	– 43%
945/961	1.044	0.055 (5.3%)	0.516	0.030 (5.9%)	– 51%
557/484	0.634	0.117 (18.5%)	0.510	0.129 (25.3%)	– 20%

CAPTIONS FOR FIGURES

Fig. 1. Diffuse reflectance FT-IR spectra of PPS-carbon prepreg obtained for different sample orientations (fibre direction with respect to instrument beam direction).

Fig. 2. Diffuse reflectance FT-IR spectra of PPS-carbon composite

Fig. 3. DSC curves of PPS-carbon prepreg and 4-ply molded panel. Scanning rate 5°C/min.

Fig. 4. Variation of IR peak height ratio (1075/1093 cm^{-1}) as a function of annealing time for PPS-carbon prepreg annealed at 105°C and 110°C.

Fig. 5. DSC curves for PPS-carbon prepreg annealed for different periods at 105°C.

Fig. 6. DSC curves for PPS-carbon prepreg annealed for different periods at 110°C.

Fig. 7. Variation of enthalpy of crystallization ΔH_c as a function of annealing time for PPS-carbon prepreg annealed at 105°C and 110°C.

Fig. 8. Relationship between IR peak height ratio and enthalpy of crystallization for PPS-carbon prepreg annealed at 105°C.

Fig. 9. Variation of IR peak height ratio for PPS-carbon prepreg annealed one hour at different temperatures.

Fig. 10. DSC curves for PPS-carbon prepreg annealed one hour at different temperatures.

Fig. 11. DSC curves for PPS-carbon prepreg heated in air at 320°C.

Fig. 12. Diffuse reflectance FT-IR spectra of PPS-carbon prepreg after heating in air at 320°C.

Fig. 13. Diffuse reflectance FT-IR spectra of PPS-carbon composite: (A) initial prepreg; (B) molded panel; (C) prepreg heated in air at 320°C, then quenched; (D) prepreg heated at 320°C, then cooled slowly.

% REFLECTANCE
0
15
30
45
60
75
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBERS
parallel
45°
perpendicular

Fig. 1

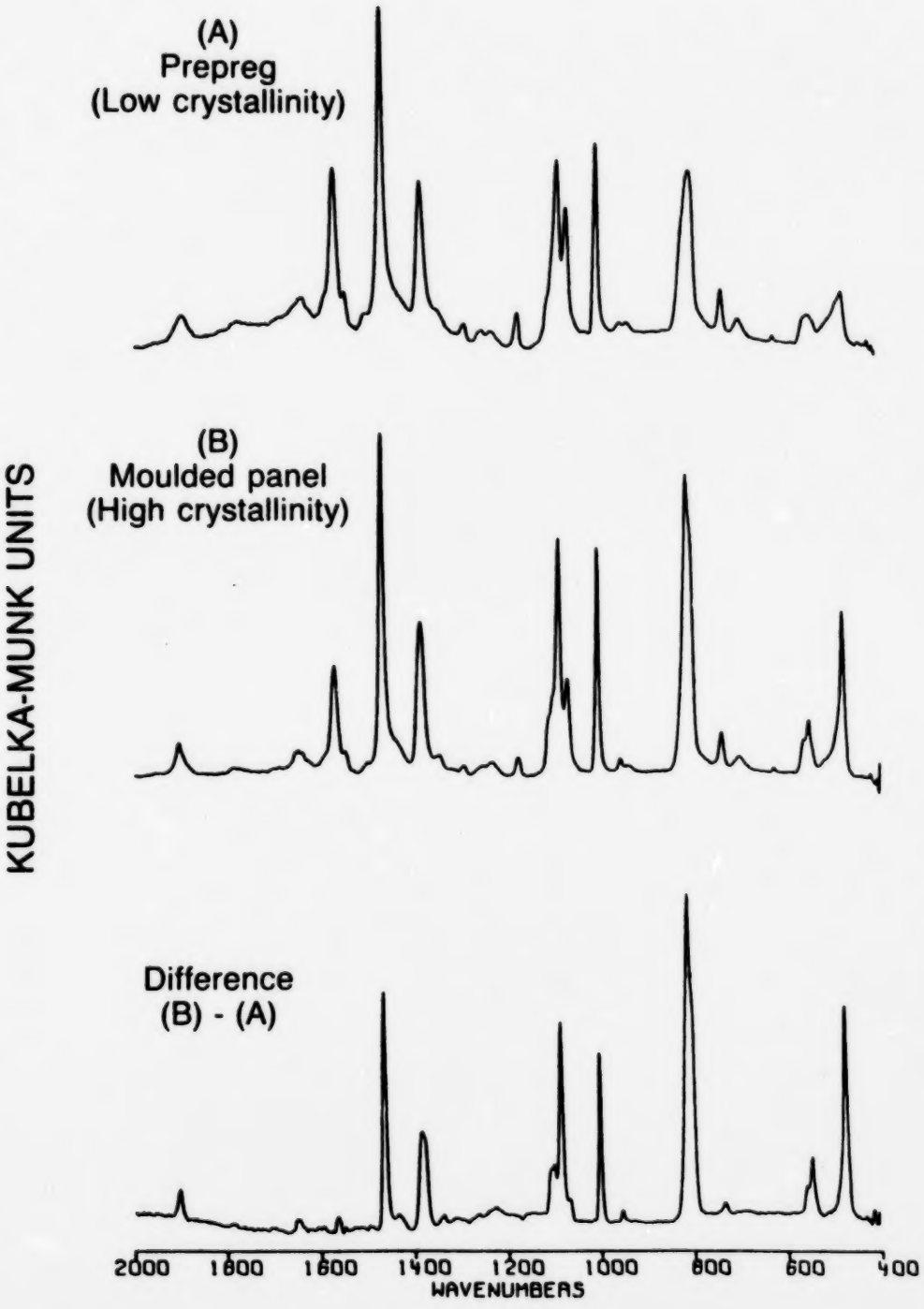
(A)
Prepreg
(Low crystallinity)
(B)
Moulded panel
(High crystallinity)
Difference
(B) - (A)
KUBELKA-MUNK UNITS
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS

Fig. 2

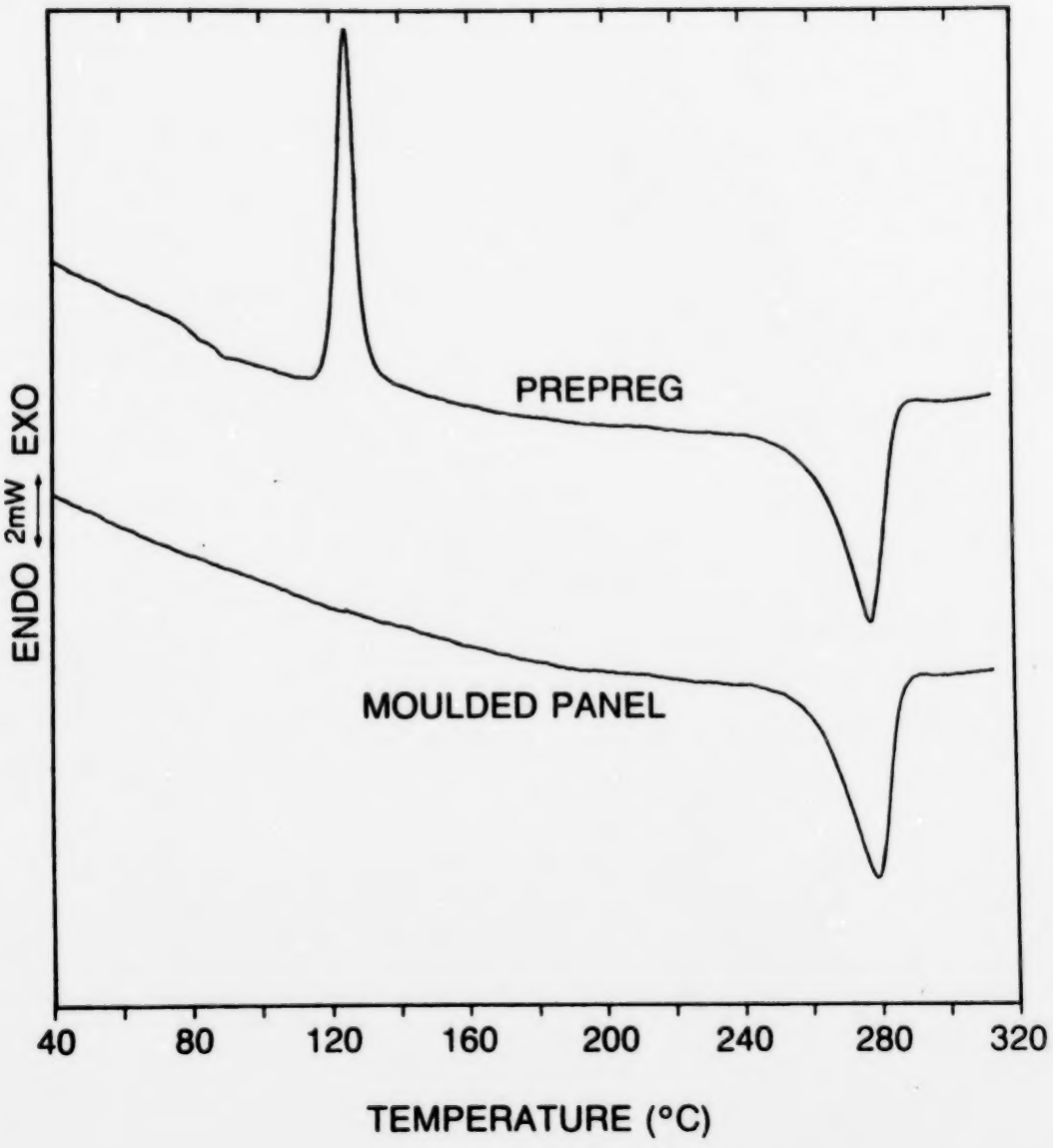
ENDO 2mW EXO
PREPREG
MOULDED PANEL
40
80
120
160
200
240
280
320
TEMPERATURE (°C)

Fig. 3

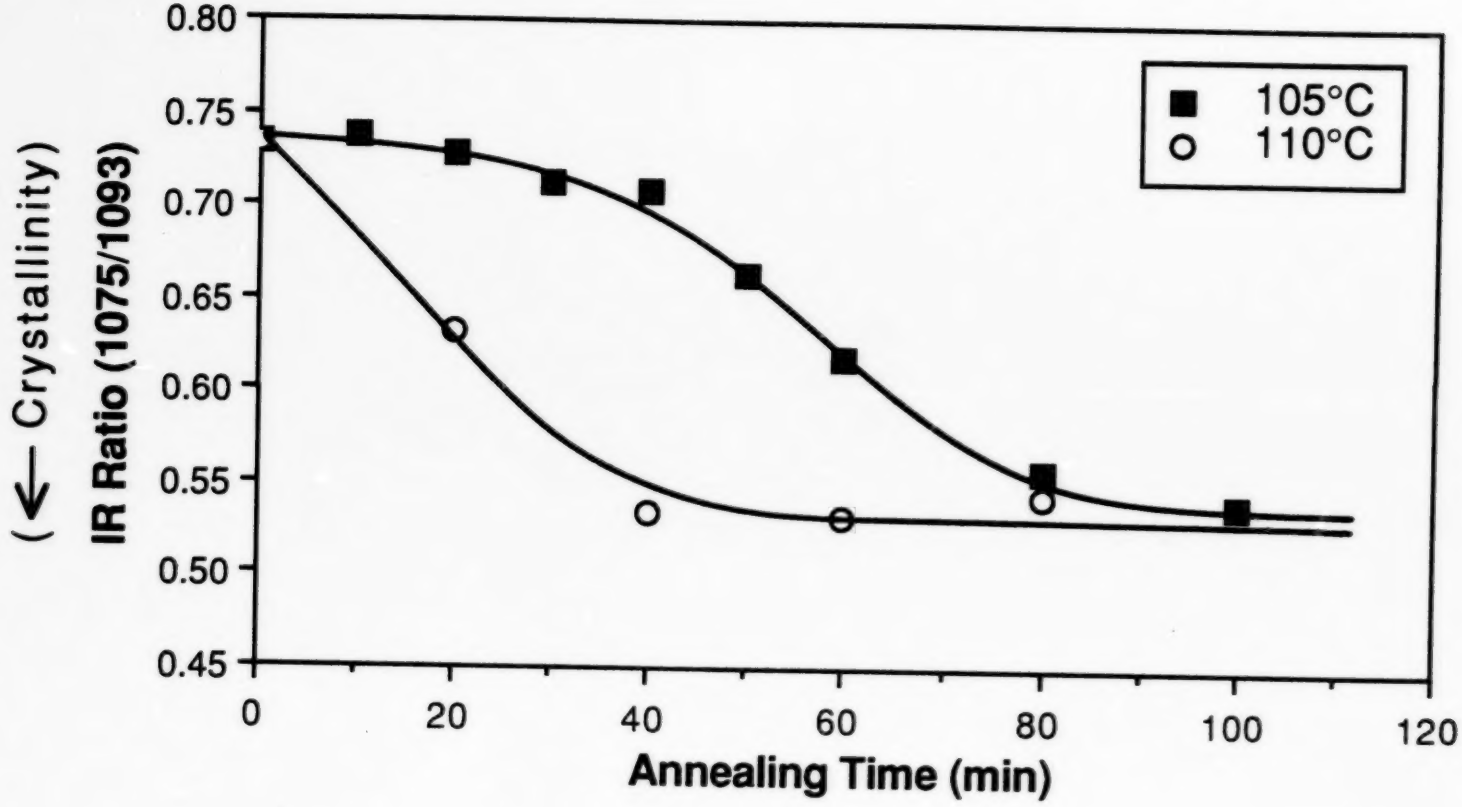
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
(← Crystallinity)
IR Ratio (1075/1093)
105°C
110°C
0
20
40
60
80
100
120
Annealing Time (min)

Fig. 4

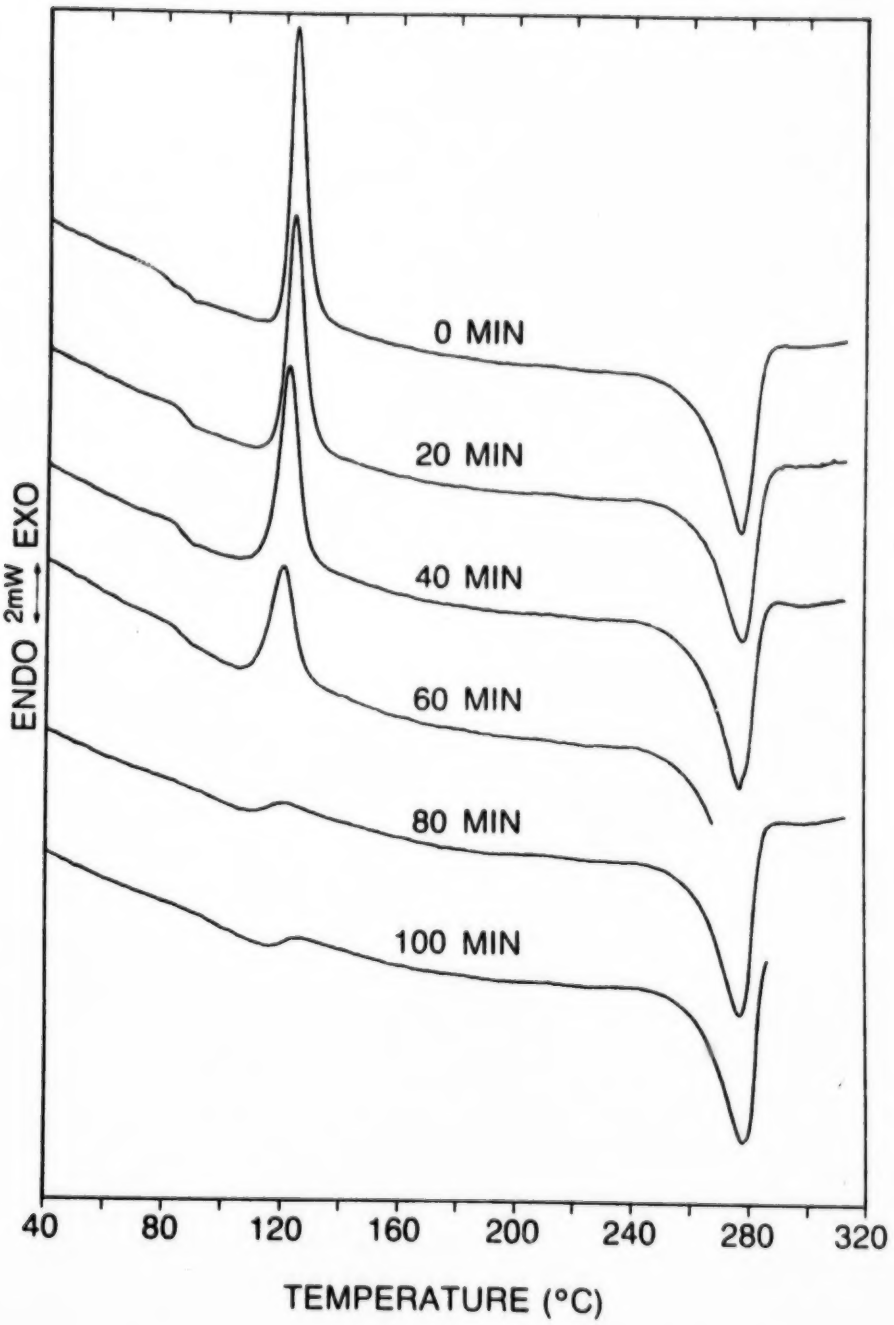
0 MIN
20 MIN
40 MIN
60 MIN
80 MIN
100 MIN
ENDO 2mW EXO
40
80
120
160
200
240
280
320
TEMPERATURE (°C)

Fig. 5

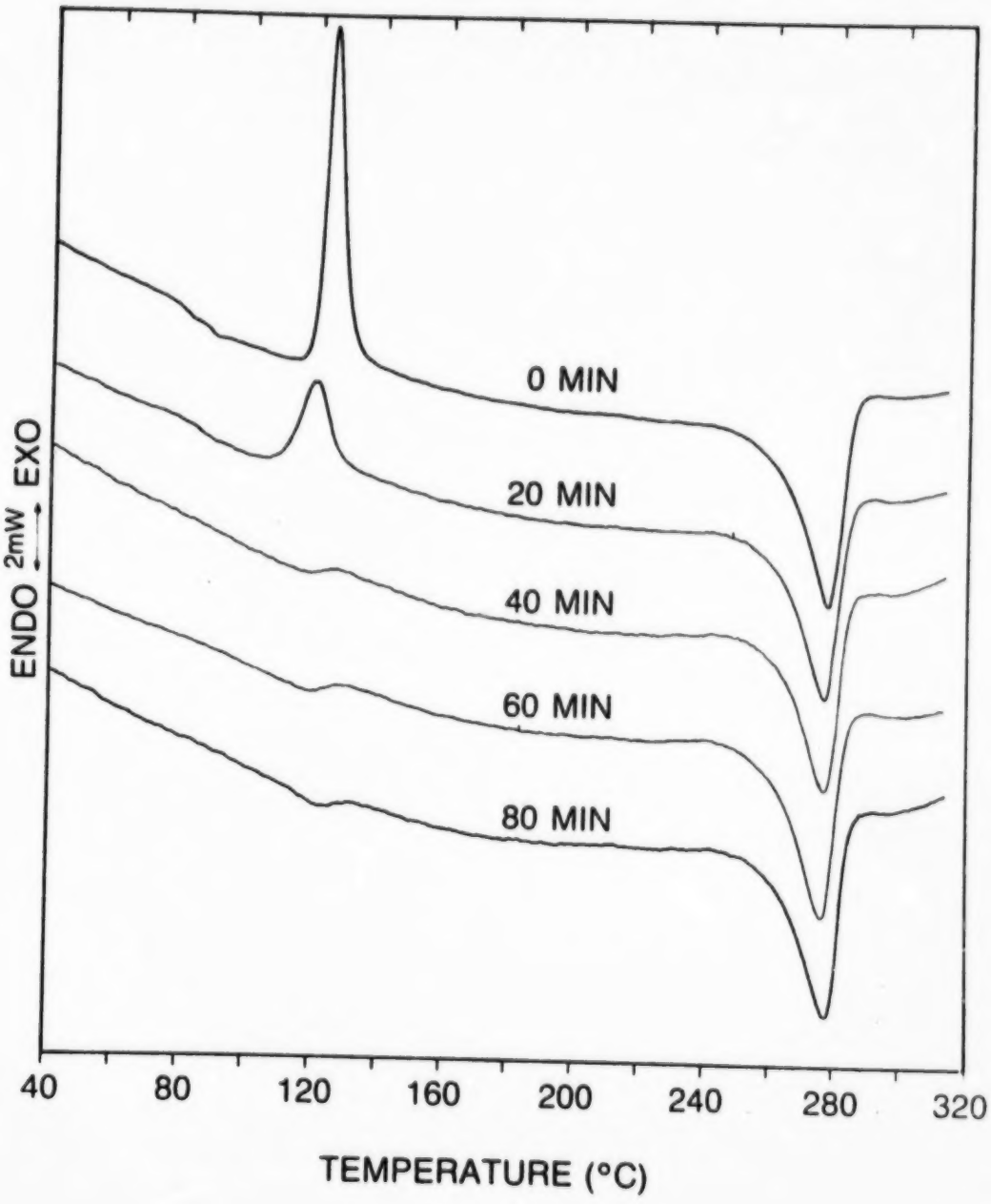
0 MIN
20 MIN
40 MIN
60 MIN
80 MIN
ENDO 2mW EXO
40
80
120
160
200
240
280
320
TEMPERATURE (°C)

Fig. 6

105°C
110°C
Annealing Time (min)
0
20
40
60
80
100
120
30
20
10
0
ΔH (crystallization) (J/g)
(← Crystallinity)

Fig. 7

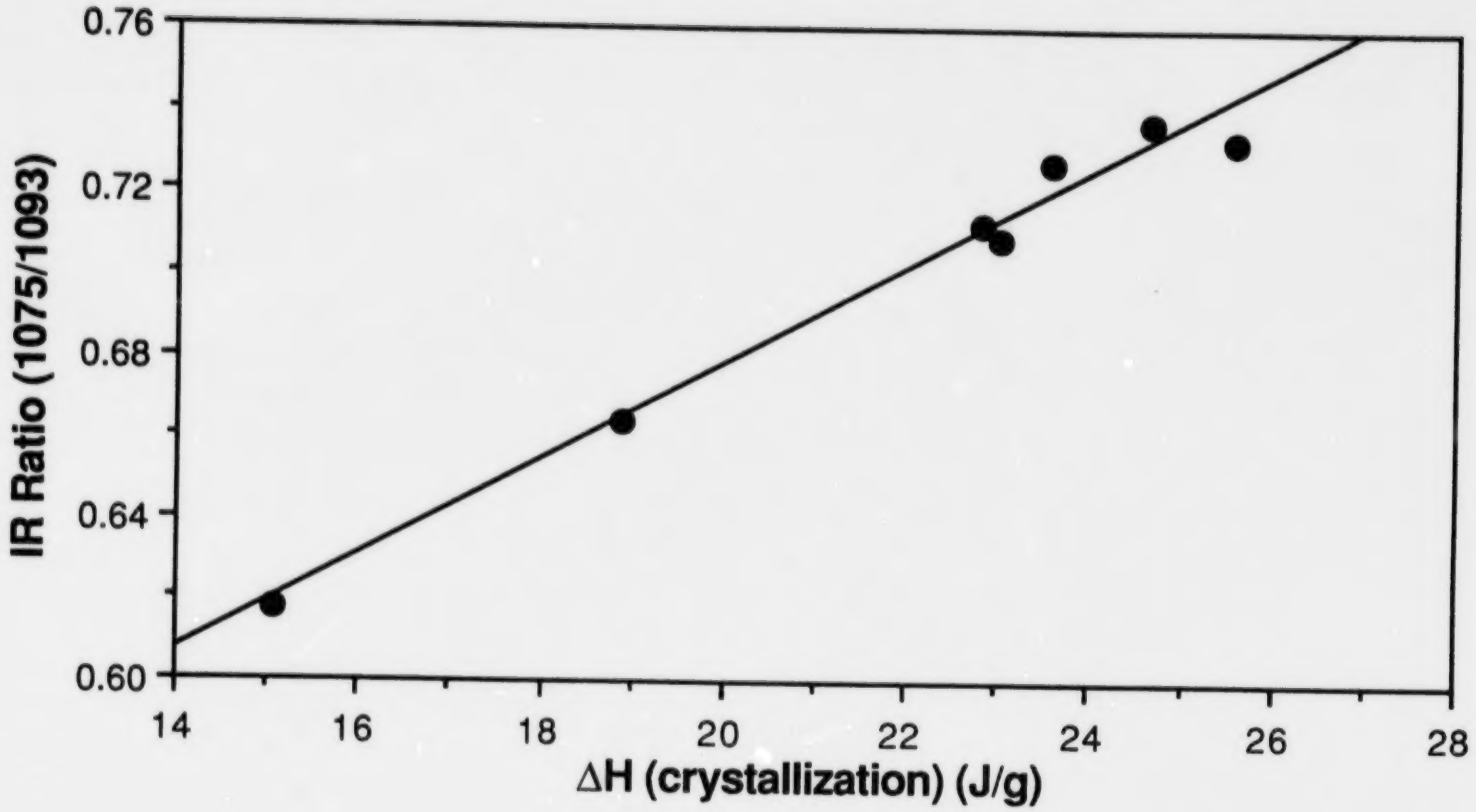
0.76
0.72
0.68
0.64
0.60
IR Ratio (1075/1093)
14
16
18
20
22
24
26
28
ΔH (crystallization) (J/g)

Fig. 8

(← Crystallinity)
IR Ratio (1075/1093)
0.8
0.7
0.6
0.5
0.4
80
100
120
140
160
180
200
Annealing Temp. (°C)

Fig. 9

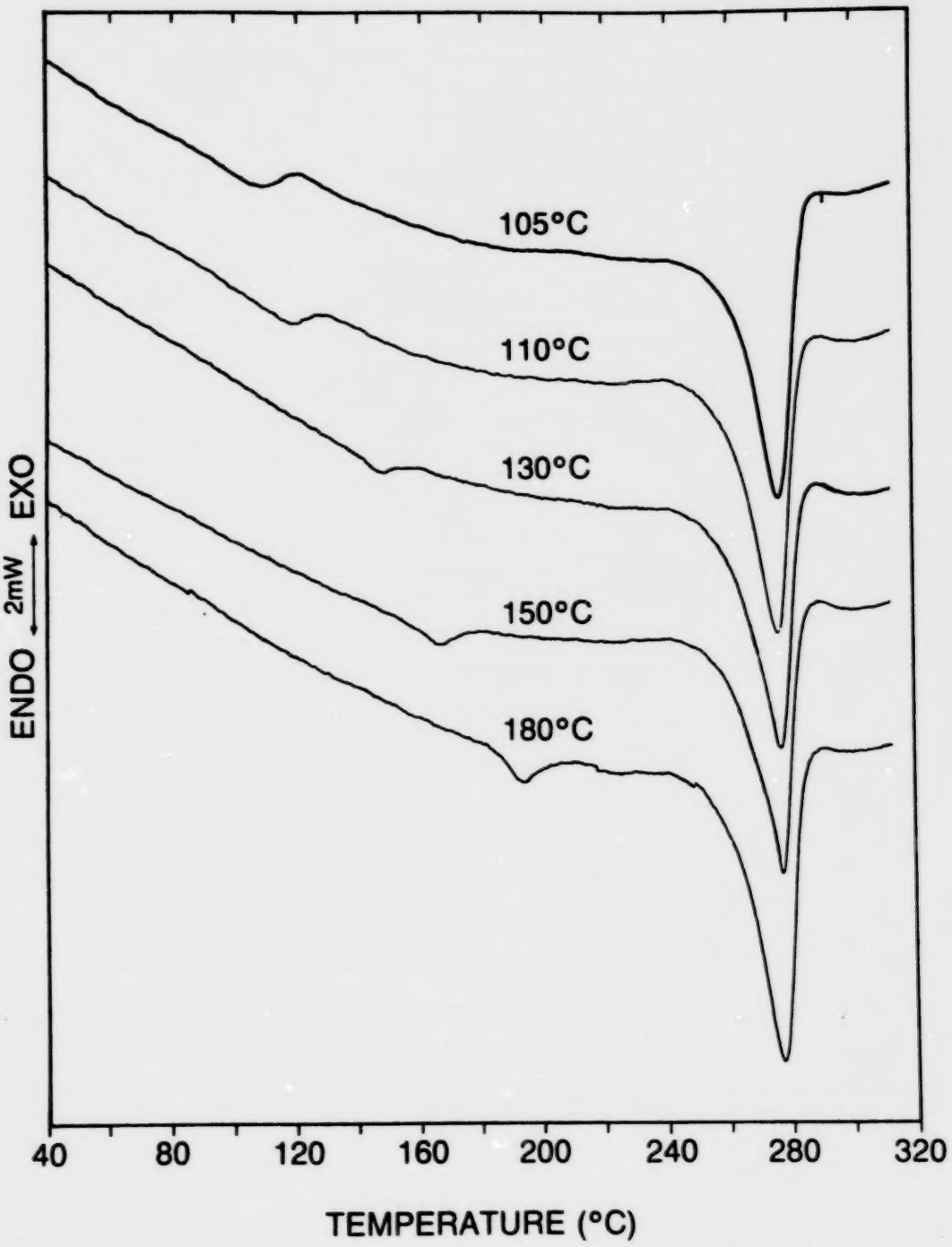
105°C
110°C
130°C
150°C
180°C
ENDO
2mW
EXO
40
80
120
160
200
240
280
320
TEMPERATURE (°C)

Fig. 10

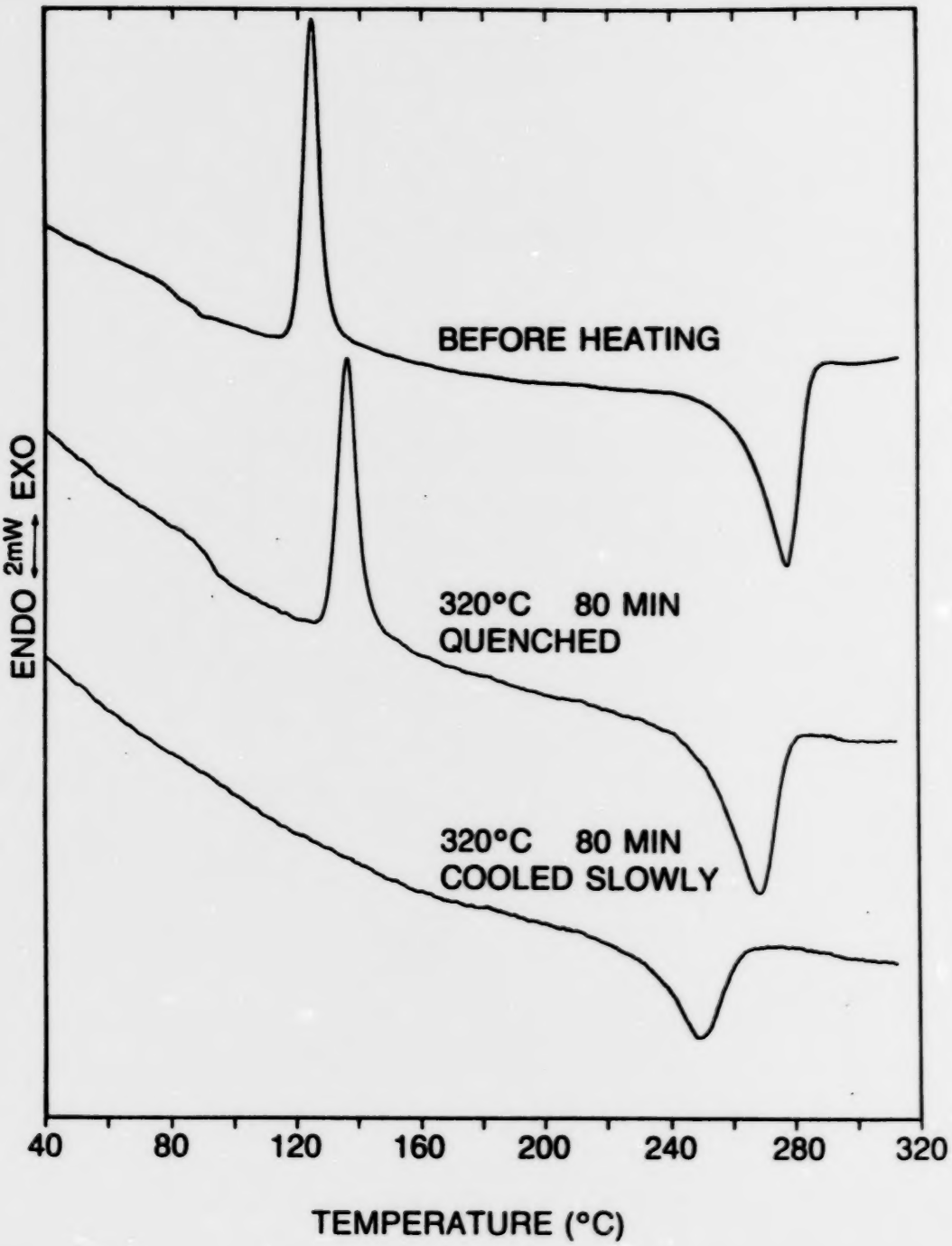
BEFORE HEATING
320°C 80 MIN
QUENCHED
320°C 80 MIN
COOLED SLOWLY
ENDO 2mW EXO
40
80
120
160
200
240
280
320
TEMPERATURE (°C)

Fig. 11

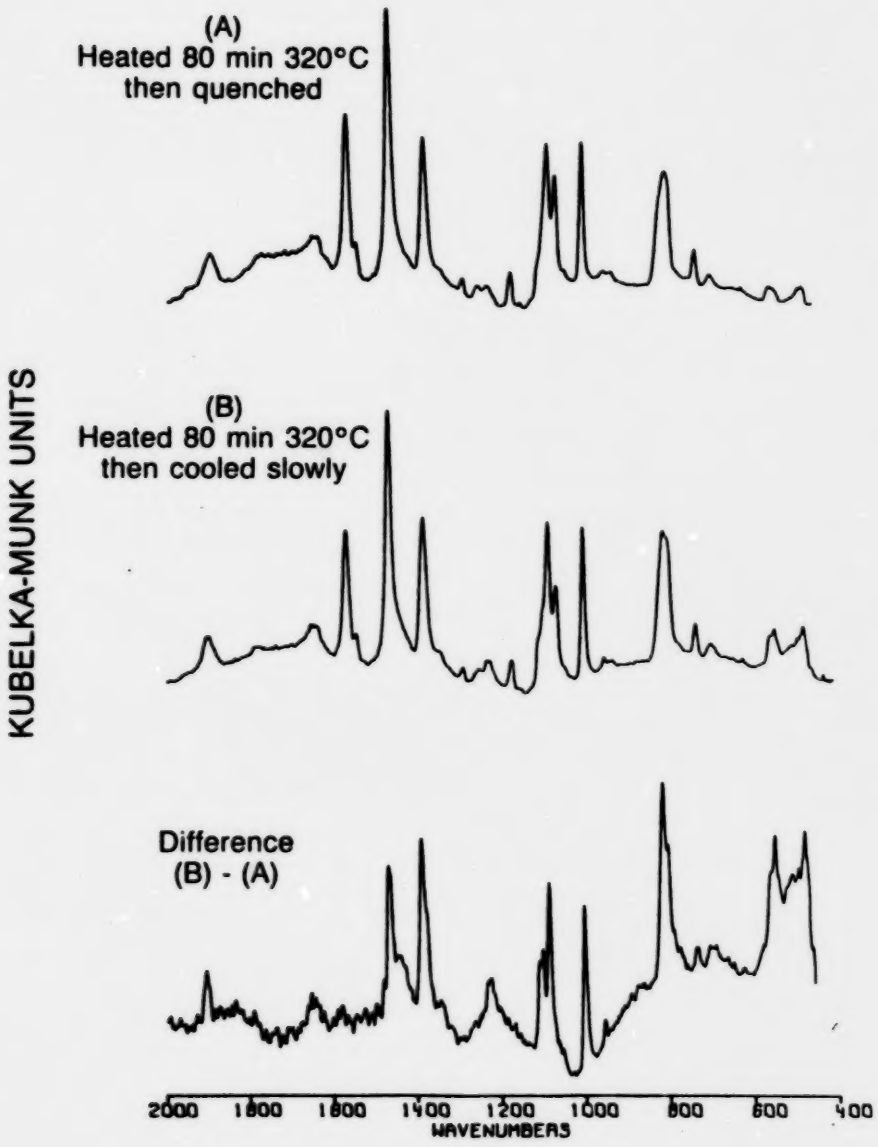
(A)
Heated 80 min 320°C
then quenched
(B)
Heated 80 min 320°C
then cooled slowly
KUBELKA-MUNK UNITS
Difference
(B) - (A)
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS

Fig. 12

KUBELKA-MUNK UNITS
(D)
(C)
(B)
(A)
800
780
760
740
720
700
680
660
640
620
600
WAVENUMBERS

Fig. 13